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Milling of peat-wood fly ash: effect on water demand of mortar and rheology of cement paste

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Abstract

The milling of fluidized bed combustion fly ashes is a promising method to improve ashes' properties as a cement replacement material. Two fly ashes from the co-combustion of peat and wood, as well as inert sand were milled at varying times. The physical properties of materials, water demand of mortar and rheology of cement paste were studied. At 25% cement replacement rate, the milling decreased the water demand of mortar by 10% and the yield stress of cement paste by 33%. It was found that milling disintegrated irregularly shaped particles, which were the main reason for high water demand of ashes, and tapped density could be used as a simple parameter to estimate the water demand for all studied materials.

Keywords: fluidized bed combustion, rheology; morphology; viscosity; correlation; packing; biomass; water requirement;

1. Introduction

To implement the principles of circular economy, industrial residues should be used as secondary resources instead of landfilling them as waste. Fluidized bed combustion fly ash (FBCFA) is one of those residues that not have established practices for utilization. One way to utilize FBCFA is to use it as a partial cement replacement material. The utilization of FBCFA has been demonstrated in several studies [1–7], and the results are promising. One challenge related to the utilization of FBCFA is that partial cement replacement is reported to increase the water demand [1,2] of the materials in their fresh state, unlike fly ash (FA) from pulverized coal

combustion, which has the opposite effect [1,8]. An increased water-to-binder ratio decreases the durability and compressive strength of concrete, but it may also be problematic in other applications where FBCFAs could be used, for example, in alkali-activated cements and materials whose strength rely solely on the hydration of the ash.

The increased water demand, which can be related to different supplementary cementitious materials, has been associated with the following material characteristics: irregular particle shape [9,10], high porosity [1], high specific surface area [2,3,9], high volume [2], high carbon content [1,4,11], high free CaO [2], high content of soluble salts [12] and other chemical factors [11]. Several of these characteristics are typically found in FBCFA. In addition, the packing density of the mixture is known to have an effect on water demand [10,13,14].

Milling of FBCFA can be done to modify the physical and mineralogical properties of FBCFA, and it has been the subject of several previous studies, e.g. [5,6,9,15–19]. However, most of these studies are done for fly ashes originating from combustion of coal and only one study [15] focuses on fly ashes which are form fluidized bed combustion of peat and biomass. The effect of milling on water demand of fly ash from fluidized bed combustion is studied only in few articles [6,9,15,16] which are mostly focused on self-hardening applications. Effect of milling of fluidized bed combustion on water demand of mortar samples, where part of cement is replaced by fly ash, is examined in two studies [6,9] which both indicated that milling of fly ash lowered the water demand. On the other hand, study of [15] showed that milling of FBCFA from combustion of peat and wood can have different effects on water demand of self-hardening samples depending on milling method and parameters. There have been also conflicting observation how milling affects to specific surface area [5,15] and bulk densities [5,16], which are both associated to water demand.

It is still unclear how well results from previous studies apply to fly ashes originating from fluidized bed combustion of peat and wood, since almost all previous studies regarding the milling of fly ash from fluidized bed combustion are done for ashes originating from coal combustion plants. These studied coal fly ashes has been substantially higher loss on ignition (LOI), which indicates to high content of unburned carbon, as well as higher content of SO_3 and CaO due to de-sulfurization with limestone injection [6,9]. According to Deschamps [17] the amount of added limestone can be 30-50 % from the mass of fuel. On the contrary, typically in the fluidized bed combustion of peat and wood there is no need to limestone injection. Therefore FBC of peat and wood can produce fly ashes, which have low contents of SO_3 and free-CaO [18]. In addition, LOI values of peat and wood FBCFA is typically low. It is likely that fluidized bed combustion of coal, together with massive amount of injected limestone, produces fly ash which chemical and physical characteristics, like morphology, differs from fly ashes of fluidized bed combustion of peat and wood. Thus, these ashes may behave differently when milled and used as a cement replacement materials. For these reasons, there is still a need for comprehensive study of the effect of milling on the water demand of mortar containing peat-wood fly ash from FBC and, to clarify how much and in what extend the physical properties effect on water demand. Therefore, for this study two FBCFA having negligible chemical effect to the water demand was chosen. These

fly ashes were originated from co-combustion of wood and peat and they were milled at different times using a tumbling ball mill and then characterized using various techniques, i.e. particle size distribution, specific surface area, packing density and particle shape. Milled sand was used as a reference material being inert in nature and having angular particle shape. The water demand of mortars containing 25% of the original and milled cement replacement materials was measured using the flow table method and was then compared with a rheological analysis of the paste samples.

2. Materials

Two FAs from wood and peat combustion were retrieved from different CFB boilers; they were not exposed to humid conditions before the experiments. The burning temperature of FA1 is around 790 °C and FA2 around 890° C. The original untreated FAs are referred to as FA1 and FA2. The sand used as a cement replacement material was milled CEN-Standard sand (CEN-Standard, Normensand GmbH) according to standard SFS-196-1:2016 [19]. The cement used in the current study was type CEM I 52,5 R- SR5 (Valkosementti, Finnsementti) according to standard SFS-EN 197-1 [20]. Aggregate sand used in this study was CEN-Standard sand (CEN-Standard, Normensand GmbH).

3. Methods

4. Results and discussion

4.1. Chemical and mineralogical characteristics of materials

Both FAs were quite similar regarding their chemical compositions (Table 3.). The amount of chloride and alkalis was low in both ashes (Table 3). The free CaO content in FA1 was 0.1% and FA2 2.9%. Both ashes contained also SO_3, FA1 3,5% and FA2 2.1%. It is known that hydration of free CaO and calcium sulfate (anhydrite and hemihydrate) consumes water rapidly, which can have adverse effects on workability. High free CaO content has been reported to increase the water demand of FBCFAs in the study of [2], but in ashes of that study contents of free CaO (4.2% and 7.2%) were much higher. Similar high contents of free CaO [6,15,23,24,18] have been reported also in other studies dealing with FBCFAs. High contents of SO_3 are reported in several studies [2,4–6,9,23]. Both FAs of this study had a low loss on ignition value, which indicates a low amount of unburned carbon. In other studies substantially higher LOI values (5.01-20%) have been reported for FBCFAs [1–6,9,25]. If all sulfur is assumed to be in the form of anhydrite, in mortar samples of this study its hydration will consume water 1.6 g and 0.9 g in FA1 and FA2 respectively (at maximum 0.6 % of used water). Hydration of free CaO in FA2 consumes approximately 1 g of water (at maximum 0,4% of used water). If we assume that all free CaO and calcium sulfate phases are hydrated rapidly during the first minutes of experiment, which may not be true in reality, their effect to water requirement can be assumed to be really low in FAs of this study. Thus it is reasonable to assume that chemical composition is not the main reason for high water demand of studied ashes. Sand was composed mainly on SiO_2 (97.2%), but it contained

99 also small amount of Al_2O_3 (1.3%). From the viewpoint of experiments used in this study, the sand can be
100 assumed to be inert material.

101 Table 3. Chemical composition of original materials

	FA1	FA2	cement	sand
CaO (%)	12.0	17.4	69.0	0.1
SiO_2 (%)	30.8	36.4	24.4	97.2
Al_2O_3 (%)	15.1	13.2	2.0	1.3
Fe_2O_3 (%)	26.7	20.2	0.3	0.4
Na_2O (%)	1.1	1.2	0.2	0.2
K_2O (%)	1.6	1.7	0.1	0.5
MgO (%)	2.5	2.1	0.6	0.1
P_2O_5 (%)	4.9	3.9	0.2	0.0
TiO_2 (%)	0.4	0.3	0.0	0.1
SO_3 (%)	3.5	2.1	2.0	0.0
Cl (%)	0.1	0.1	0.0	0.1
Free CaO (%)	0.1	2.9	NA	NA
Loss on ignition 950 °C (%)	1.5	0.6	1.2	0.3

102

103 According to XRD analysis, both FAs of this study contained some common mineral phases, such as anhydrite,
104 anorthite, magnetite and quartz (Fig 1). In addition to these, FA1 contained also small amount of kupletskite
105 (Fig 1 and Table 4) while FA2 contained some paravauxite and lime. FA1 contained also significant amount
106 of aluminum phosphate (9.3 %) while in FA2 amount was really low (0.7 %) (Table 4). Amount of unidentified
107 material, which includes also amorphous material was 44.3 and 67.7 % in FA1 and FA2 respectively (Table
108 4). Cement consisted mainly from alite, belite and gypsum, which are typical phases in Portland cement as
109 well as some chlorellestadite and farringtonite (Fig1). According to XRD analysis, amount of gypsum was
110 suspiciously high (8.5%) (Table 4) but this may be due to uncertainty to used analysis method.

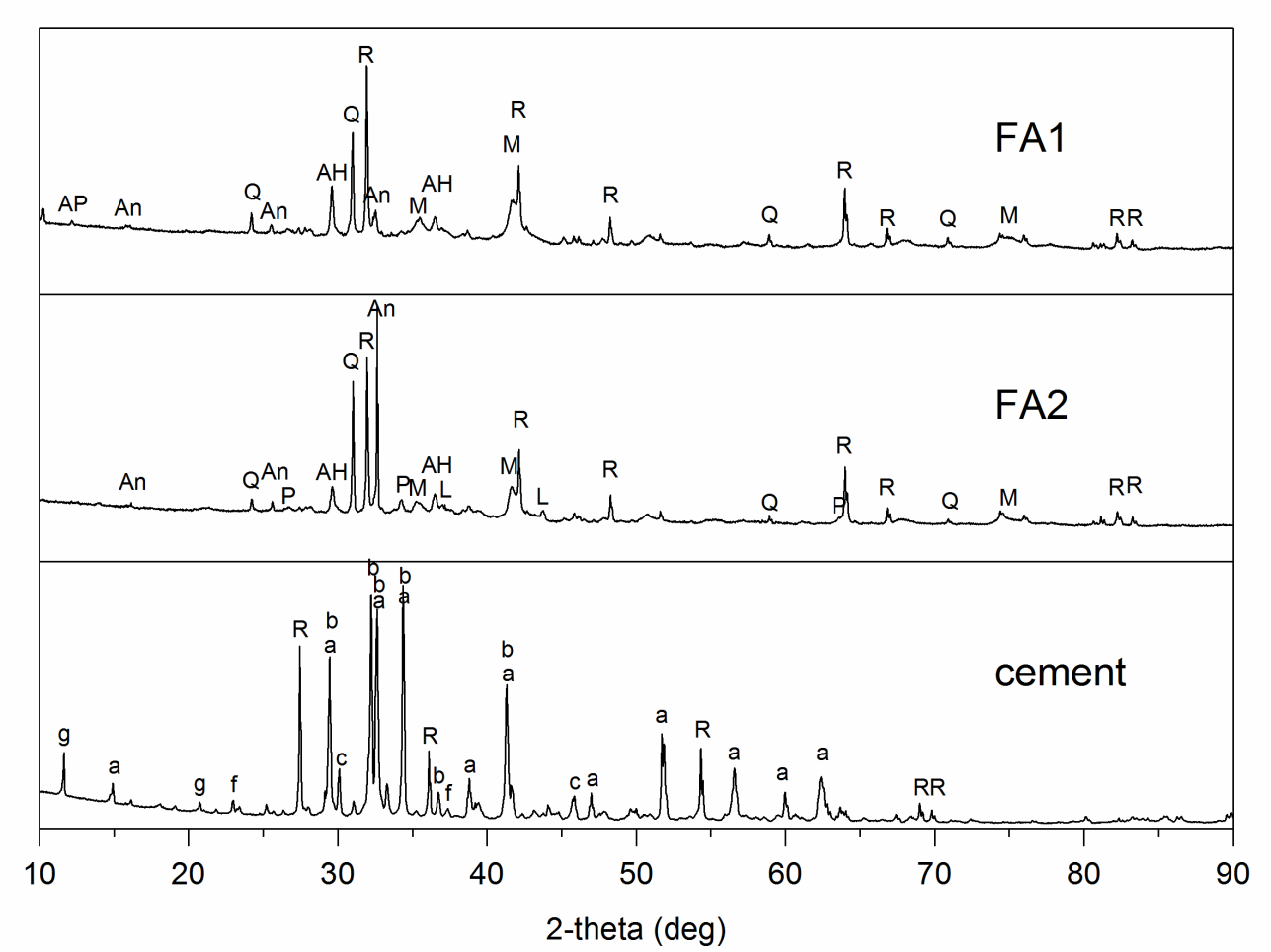


Figure 1. XRD graphs of FA1, FA2 and cement: Ah = anhydrite, An = anorthite, AP = aluminum phosphate, L = lime, M = magnetite, P = paravauxite, R = Rutile, Q = quartz, a = alite, b = belite, c = chlorellestadite, f = farringtonite, g = gypsum

Table 4. Phase composition of FA1, FA2 and cement

	FA1	FA2	cement
aluminium phosphate (%)	9.3	0.7	-
anhydrite (%)	5.5	2.1	-
anorthite (%)	5.5	5.9	-
kupletskite (%)	2.1	-	-
lime (%)	-	2.2	-
magnetite (%)	27.3	11.5	-
paravauxite (%)	-	5.8	-
quartz (%)	6.2	4.2	-
alite (%)	-	-	54.4
belite (%)	-	-	16.7
chlorellestadite (%)	-	-	5.4
farringtonite (%)	-	-	2.3
gypsum (%)	-	-	8.5
unidentified and amophous (%)	44.3	67.7	8.9

4.2. Effect of milling on particle characteristics

4.2.1 Morphology

The original FAs possessed a radically different morphology than cement and sand, which can be seen by comparing the FESEM pictures of the original ashes (Fig. 2a and b) to pictures of the cement and sand-180 (Fig. 2e and f). For FAs, at least three different particle types can be distinguished: spherical particles, angular particles, and irregularly shaped particles (Fig. 2a and b). The spherical particles are associated to melting of ash particles in high temperatures [26,27] which can form amorphous glassy phases. The large angular particles could originate from bed material or from impurities originating in fuel [27]. Irregularly shaped particles consist probably from unburned fuel that has not melted to form spherical particles [28], irregularly shaped particles are typical for FBCFAs because the temperature in the combustion process is relatively low. Additionally, some ash particles resemble particles of diatomaceous earth, which could migrate with the peat into combustion process. All these particle types can be seen in both ashes, but their share differs between the ashes. The amount of the different particle types is hard to quantify, but based on the FESEM images, it can be concluded that FA1 contains more flaky particles while FA2 has a higher share of spherical particles. The higher share of spherical particles in FA2 could be explained by higher burning temperature. It seems that in the ashes of this study irregularly shaped particles are not associated to unburned carbon, since LOI values of both ashes were low.

The effect of 90 min of milling on FA1 and FA2 is presented in Fig. 2c and d. Interestingly, milling seems to affect mainly irregularly shaped particles, which can be seen by comparing the FESEM images of the original and milled ashes. In the original ashes, it can be seen that large irregular particles often have a diameter of tens of micrometers. During milling, these low-density particles are quite rapidly shattered, producing a diameter below 10 µm, and only the remains of these irregularly shaped particles can be seen after milling. On the contrary, spherical ash particles and angular sand particles were less affected by milling. In the original ashes, the diameter of the spherical particles typically ranged from a few to 50 microns while the diameters of sand particles range from a few to 100 microns. Even after 60 and 90 min of milling, many spherical ash particles remained intact, especially at the case FA2, where their share is higher than in FA1. In similar way, many large angular particles still existed in the milled ashes. The reason for this could be the large share of small, irregularly shaped particles protecting stronger angular and spherical particles due to the agglomeration effect. Similar observation was reported in other study [29] where cement clinker was ground together fluidized bed combustion filter ash; ash impeded the disintegration of clinker grains. It is possible that grinding balls and bigger particles are coated with smaller particles, which reduces the milling efficiency. Grinding aids and the effect of grinding media size are of interest for our future studies.

The FESEM images of sand, contrary to the FAs, showed that the sand had a similar dense morphology as the cement, and no changes in the morphology was observed among 60, 120, and 180 min milled samples; here, only particle size seemed to change. However, it is possible that the original sand possessed a smoother particle shape, and milling crushed these particles into the jagged fragments seen in the FESEM images.

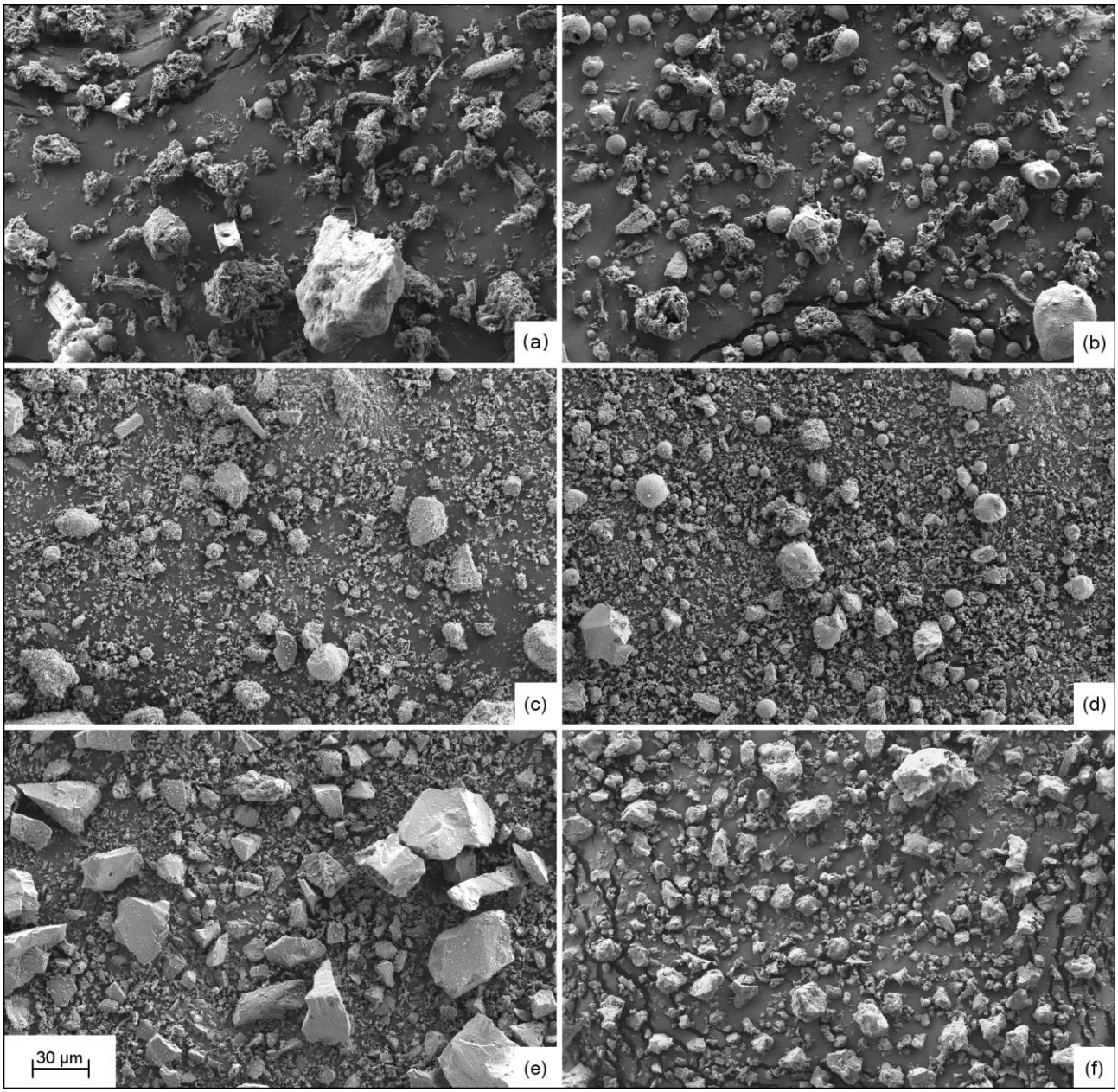


Figure 2. FESEM images of materials: (a) FA1; (b) FA2; (C) FA1-90; (d) FA2-90; (e) sand-180; (f) cement.

4.2.2. Particle size distribution

Milling had a clear effect on particle size distribution of materials especially at the first stages (Fig. 3). However, when milling times were extended beyond certain limit, effects to particle size distribution were negligible. In the case of FAs the limit was approximately at 60 min and for sand limit seemed to be 120 min.

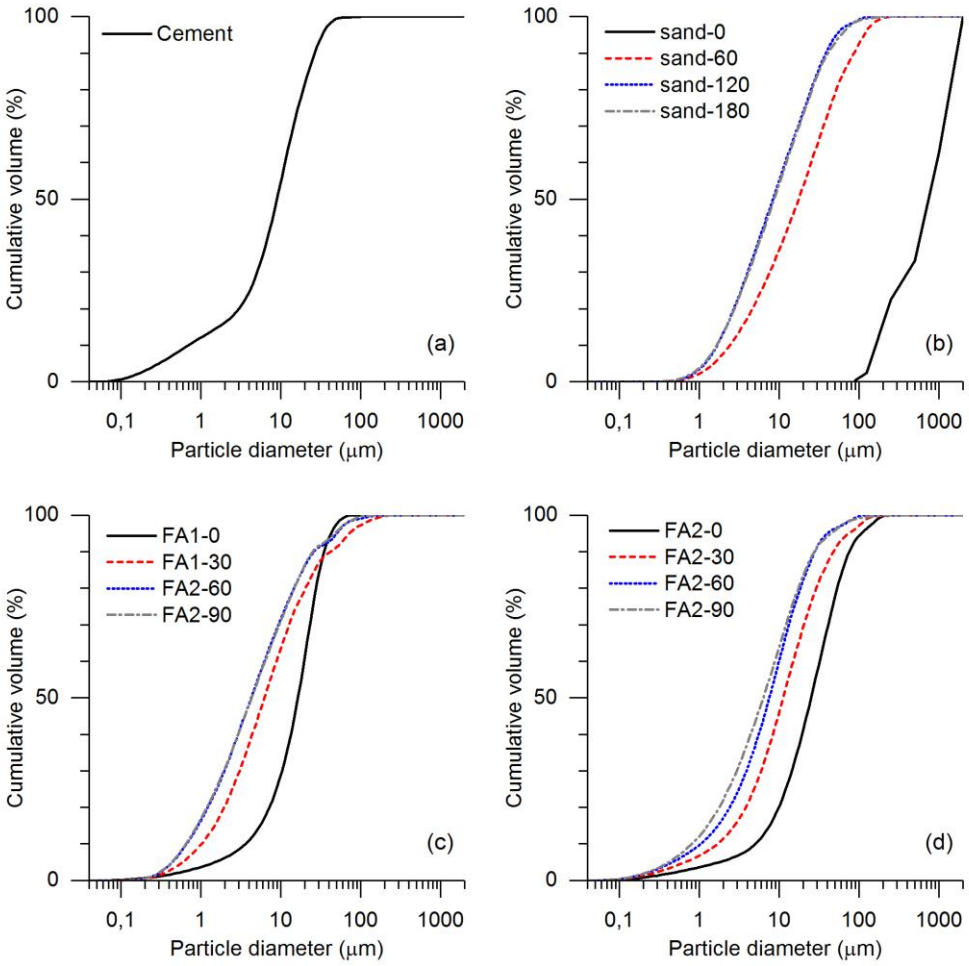


Figure 3. Cumulative particle size distributions of materials. (a) cement; (b) sand; (c) FA1; (d) FA2.

Both FAs originally had a higher median particle size than cement, but 30 min of milling decreased the particle size to the same median particle size range as the cement, 7.9 μm (Fig. 4a). After 30 min of milling, changes in the median particle sizes of ashes were small. Similarly, Fig. 4a shows that sand initially had a much higher median particle size than in the ashes, but 60 min of milling was enough to bring the median size down to the same range as the ashes. When sand was milled for 120 min, it reached almost the same median particle size as cement. When milling was continued for 180 min, there was no further reduction in the median particle size.

It seems that all materials eventually reached a level where additional milling had only a small effect on particle size and where a further decrease in particle size would probably require smaller grinding media and addition of grinding aids.

Milling clearly increased the span of particle size distribution of every material (Fig. 4b). The span of FA1, which originally had the smallest span of the studied materials, increased first significantly, but then started to slowly decrease as milling continued over 30 min. In the case of FA2 the span first increased from 2.8 to 4.1. When milling was continued to 60 min, span decreases a little bit to 3.6, and finally, after 90 min milling,

reached value of 4.2. Similarly at the beginning, milling increased also the span of particle size distribution of sand. However, changes in particle size distribution were quite small after initial increase.

4.2.4. Specific surface area

Milling increased the specific surface area of all the materials but to a varying degree (Fig. 4c). Figure 4c shows that the specific surface area of FAs is much higher than those of cement and sand. In the case of FAs, milling mainly affected the highly irregularly shaped ash particles and agglomerates, which already possessed a high surface area; therefore, the surface area increase was only moderate (15% for FA1 and 16% for FA2 after 90 min milling). The results of these experiments are in line with the study of [15], in which ball milling had no significant effect on specific surface area, but the results conflict with the studies of [5,16], in which ball milling significantly increased the surface area of FBC fly ash.

In contrast to FAs, original sand had low specific surface area (0,50 m2/g) but milling increased it significantly (Fig. 2c). Highest value (2,1 m2/g) was achieved after 120 min milling and when milling was continued to 180 min specific surface area for some reason slightly decreased. The higher relative increase in specific surface area in the case sand is related to more solid particle shape, meaning that new surface area created in milling is significant compared to original surface area.

4.2.5. Tapped density

Milling gradually increased the tapped densities of the FAs, but the effect on sand was the opposite (Fig 4d). Originally, FA1 and FA2 both had very low tapped densities of 379 and 698 kg/m^3, respectively. Although 90 min of milling gradually increased the tapped densities of FA1 and FA2 by 168% and 54%, respectively, their densities still remained below the tapped density of cement, 1286 kg/m^3. Changes in the tapped densities of ashes can be explained by the disintegration of large flaky particles into smaller particles that can then form a denser system due to lower in-particle porosity and closer to optimal particle packing. Similar observations are reported elsewhere for FBCFAs [5], as well as for ceramic suspensions [30]. However study of Chen et al.[16] reported that milling of FBCFA from combustion coal had only negligible effect on tap density of fly ash, during 60 min of milling tap density increased from original 1.27 to 1.33 g/cm^3.

The tapped density of sand was initially 1952 kg/m^3, and 120 min of milling decreased the tapped density of sand from its original by 35%, to almost the same value as cement. However, further milling did not had much of any effect on the tapped density of sand. A decrease in the tapped density of sand could be explained by the increase of inter-particle forces and changes in the particles' packing due to changes in PSD and particle shape. It is possible that the original sand particles had more rounded shape with lower inter-particle friction and a higher density due to more optimal particle packing.

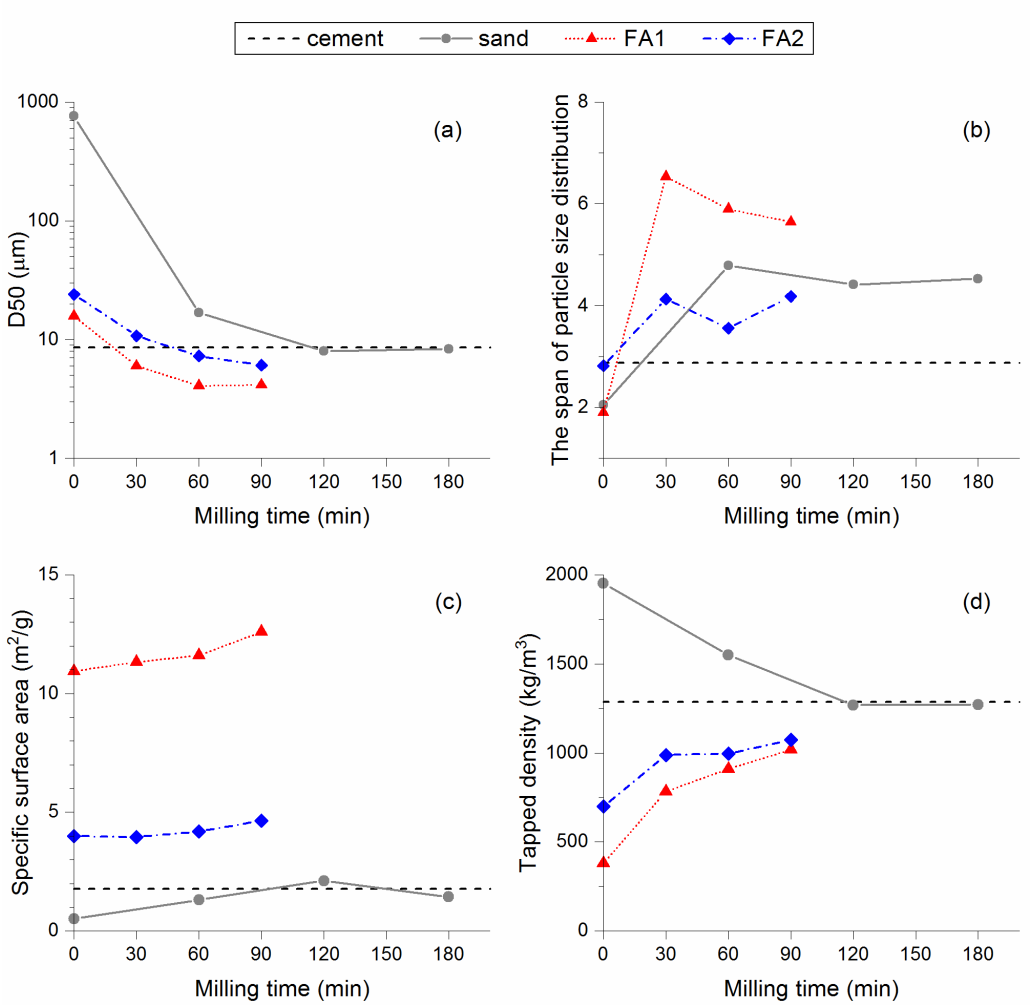


Figure 4. The effect of milling time on the characteristics of cement replacement materials. (a) Effect on the median particle size (µm); (b) effect on the span of the particle size distribution; (c) effect on the specific surface area (m^2/g); (d) effect on the tapped density (kg/m^3).

4.3. Effect of milling on water demand

Partial cement replacement with FA1 led to a clear increase in water demand, but milling was able to partly mitigated this (Table 5). When un-milled FA1 was used, the water demand was 129%. However, milling gradually decreased the water demand, and the lowest value of 116% was achieved with the highest milling time (FA1-90). In other words, 90 min of milling dropped the water-to-powder ratio from 0.64 to 0.58 (i.e., by 9.4%) in mortars where 25% of the cement was replaced using FA1. The use of FA2 similarly increased water demand but not as much as FA1 (Table 5), and milling was only helpful up to a certain point. The water demand of the sample with the original FA2 was 116%. Milling decreased the water demand gradually,

showing the minimum value of 107% with 60 min of milling time. With further milling, for some unknown reason water demand increased to 113%.

The water demand of milled sand was essentially the same as in the control sample, and it remained constant, regardless of different milling times (Table 5). However, the flow table method was insensitive to small changes in workability because the water demand value was accepted when the spread value of a test sample reached ± 10 mm from the control sample. Thus, different test samples can have the same water demand value even though they may have slightly different spread values. When the diameters of the spread mortars were compared, the spread diameters of the samples M-sand-60 and M-sand-120 were very close to the control sample, which had a diameter of 17.66 cm. However, the spread diameter of sample M-sand-180 differed a little more from the control sample, which indicates that the mortar is actually slightly stiffer than the control.

Table 5. Results of water demand measurements using a 25% replacement rate.

Sample	Added water (g)	Water-to-powder ratio	Spread mortar diameter (cm)	Water demand (%)
M-control	225	0.50	17.66[a]	100
M-sand-60	225	0.50	17.26	100
M-sand-120	225	0.50	17.68	100
M-sand-180	225	0.50	16.89	100
M-FA1	290	0.64	17.66	129
M-FA1-30	275	0.61	17.27	122
M-FA1-60	268	0.60	17.60	119
M-FA1-90	260	0.58	17.29	116
M-FA2	260	0.58	17.91	116
M-FA2-30	257	0.57	17.87	114
M-FA2-60	240	0.53	17.47	107
M-FA2-90	255	0.57	17.91	113

[a] The diameter in which the test samples were compared

In other studies where FBCFAs from coal combustion are milled results have been similar with this study. In the study of Li et al. [6] 50 min milling decreased water demand from 122 to 109 % and in the study of Fu at al. [9] 50 min milling decreased water demand from 122 to 107%. When slightly higher cement replacement rate of before mentioned studies is taken in to account, it can be concluded that FA1 had significantly higher water demand than in those fly ashes from coal combustion while water demand of FA2 was approximately at the same level. It is not surprising that FA1 containing mortars had a higher water demand than FA2 containing mortars. Although both FAs originate from fluidized bed combustion, FA2 contains a significant amount of spherical ash particles, which are more typical for FAs from the combustion of pulverized fuels. Spherical particles can also be found in FA1, but their proportions seem to be significantly lower compared to FA2. When ashes are milled for 60 min, large, flaky particles were disintegrated. The particles of milled sand are clearly angular, regardless of the milling time, and their effect on water demand is very close to cement.

4.4. Effect of milling on rheology of cement paste

Although the flow table method can be used to assess the water demand of the samples, fundamentally, it cannot uncover the underlying phenomena. Therefore, yield stress and viscosity of the samples was studied to gain a deeper understanding of the effects of milling. Cement paste samples with 25% replacement and constant water-to-binder ratio were used.

FA1 increased both the yield stress and viscosity of cement paste significantly (Table 6). However, in this case, the milling time of the material had a clear effect on the rheology. Without milling, relative to the control sample, FA1 increased the yield stress of paste by 533% and viscosity by 607%. When 30-min-milled FA1 was used instead of the original FA1, the yield stress decreased from 54.4 Pa to 43.8, and viscosity form 5.23 to 3.58. A milling time of 60 min decreased the yield stress even further to 38.5 Pa and viscosity to 2.14 Pa·s. When the milling time of FA1 was increased to 90 min, the yield stress decreased only by 6% while the viscosity decreased 10%. Herschel-Bulkley model's flow index for original FA1 was 0.58 which was really close to control sample (0.59), but 30 min millig decreased flow index to 0.46. After 60 and 90 min milling flow rate index reached values of 0.52 and 0.51.

Cement replacement using FA2 also increased both the yield stress and viscosity significantly but not as much as for FA1 (Table 6). The original FA2 showed a 165% increase in yield stress and 157% increase in viscosity when compared to the control sample. Also, 30 min of milling for FA2 decreased both yield stress and viscosity by 31%. Further milling of FA2 had only minor impacts on the yield stress, but after 60 min milling viscosity dropped to 1.21 Pa·s and 90 min milling brought viscosity down to 1.07 Pa·s, which was 45% higher than the viscosity of the control sample. Original FA2 had floe index of 0.72, which was the highest f analyzed samples. Milling decreased the flow index so that after 60 min milling value was 0.52 and additional milling had only negligible effect.

When the cement was partly replaced using milled sand, it did not have dramatic effects on the viscosity or yield stress, regardless of the milling time (Table 6). P-sand-60 had slightly lower yield stress and 34% lower viscosity than the control while samples P-sand-120 and P-sand-180 had almost identical yield stresses and viscosities as the control. Milling of sand seemed to slightly decrease the flow rate index.

Table 6. Effect of studied cement replacement materials on the yield stress (Pa), viscosity (Pas) and Herschel-Bulkley flow index of cement paste samples at a cement replacement rate of 25%.

Sample	Yield stress (Pa)	Apparent viscosity (Pa·s)	Herschel-Bulkley flow index
P-control	8.6	0.74	0.59
P-sand-60	6.4	0.49	0.61
P-sand-120	10.5	0.78	0.56
P-sand-180	10.1	0.77	0.57
P-FA1	54.4	5.23	0.58
P-FA1-30	43.8	3.58	0.46
P-FA1-60	38.5	2.14	0.52
P-FA1-90	36.3	1.93	0.51
P-FA2	22.7	1.90	0.72
P-FA2-30	15.6	1.31	0.58
P-FA2-60	15.2	1.21	0.55
P-FA2-90	15.5	1.07	0.56

Interestingly rheological analysis showed greater differences between samples than water demand experiments. One reason for this could be the absence of sand which plays significant role in the rheology of mortar samples. It is possible that inclusion of bigger aggregates in concrete scale could even further reduce the difference in performance between different cement replacement materials.

4.5. Correlation of water demand and rheological properties with replacement material characteristics

To identify the material characteristic that had the most dominant effect on the water demand of the mortar, a correlation between the different replacement material characteristics (i.e. particle size distribution, BET, tapped density) with water demand, yield stress and viscosity was studied. Figure 5 shows how the median particle size, span, specific surface area, and tapped density correlate with water demand, yield stress, and viscosity.

Tapped density was identified as the most accurate measure of quality; it correlated well with water demand ($R^2 = 0.82$) and moderately well with yield stress ($R^2 = 0.70$) and viscosity ($R^2 = 0.78$). This was true when the data were aggregated to contain all the samples, as well as within single data sets, except in the case correlation between tapped density and water demand case of FA2 (Fig. 5j, k, and l). This indicates that an increase in the tapped density of the replacement materials can lead to a decrease in water demand, yield stress, and viscosity and hence could be used as simple quality control measure in FAs.

The results of this study indicate that the low packing density of the original FAs, which was caused by the high share of irregularly shaped ash particles, was the main reason for their poor properties. Interestingly, milling can significantly increase the packing density of FAs by shattering large, irregularly shaped ash

particles into smaller particles. This decreases the amount of water required to fill the spaces between ash particles, and more water is then available to lubricate the paste, which consequently leads to a lower yield stress and viscosity.

The specific surface area of materials had a good positive correlation with yield stress (R^2 = 0.86), moderate positive correlation with water demand (R^2 = 0.67) and some positive correlation with viscosity (R^2 = 0.55) (Fig. 5g, h, and i). However there was no similar correlation within the data sets. In the case of FA1, the specific surface area was negatively correlated with both water demand, yield stress and viscosity. The specific surface area of FA2 showed weak negative correlation with viscosity and no correlation with water demand and yield stress. For sand, specific surface area showed weak positive correlation with yield stress and viscosity but no correlation with water demand.

The results of this study suggest that although milling slightly increases the specific surface area of FBCFA, it does not have adverse effects on water demand, yield stress or viscosity. This observation is in line with study of [10], in which it was observed that the specific surface area did not correlate with water demand when the materials consisted of highly irregularly shaped particles. It can be concluded that although water demand and yield stress correlate well with specific surface area, it may not be the primary reason for the high water demand of samples where FAs are used.

It is well known that the particle size distribution of materials has an effect on their packing density. In an ideal case, a well-graded particle size distribution enables smaller particles to fill the voids between bigger particles, leading to denser packing. Within individual materials median particle size and span of particle size distribution indeed showed correlation with water demand, yield stress and viscosity (Fig. 5a-f) indicating that increase in the span of particle size and decrease in median particle size would lower the water demand, yield stress and viscosity. In the case of FAs correlation was moderate, except correlation between span and water demand of FA2, and in the case of milled sand correlation was good, except correlations with water demand. However, when data from all the samples were combined, neither the median particle size nor the span of particle size distribution of the studied materials correlated with water demand, yield stress, or viscosity (Fig. 5a-f). Thus it seems that span of particle size distribution and median particle size are not very useful parameters to estimate how random fine material affects to water demand and rheology.

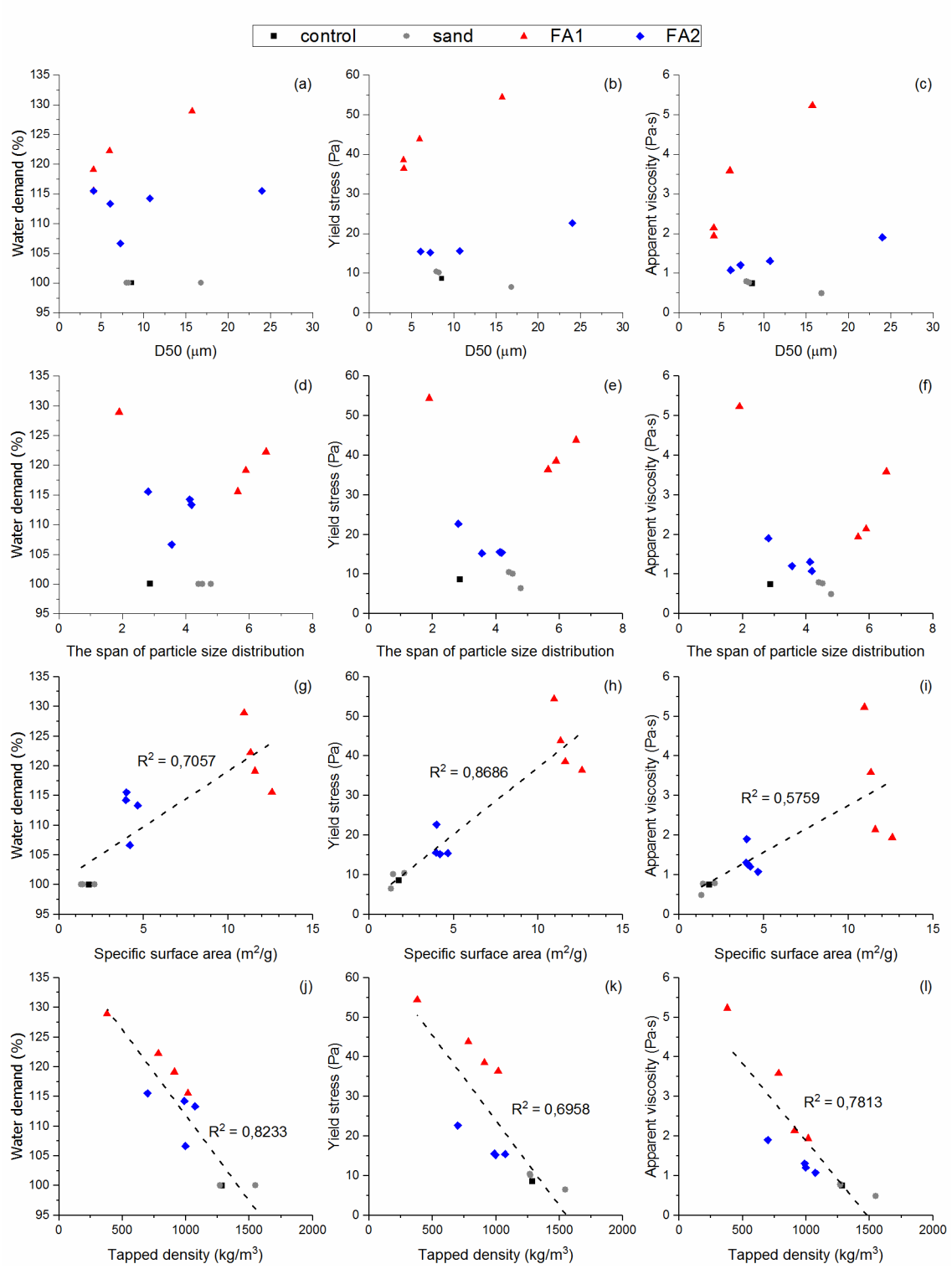


Figure 5. Correlation between consistency and ash characteristics.

4.1. Possibility of replacing cement with fly ashes from FBC

Based on these results, it is clear that milling both types of FAs had a positive effect on the water demand of the mortar samples, as well as on the yield stress and viscosity of the paste samples. Milling can significantly

improve the packing of ashes, but it cannot eliminate all the negative effects of irregularly shaped particles. It is possible that using grinding aids could improve the effect of milling even further [5], but even without the use of grinding aids, milling FBCFAs from peat and wood combustion seems to be an effective way to improve the properties of these type of ashes. If FAs are used as self-cementitious materials [15], the positive effect of grinding would be even higher because the binder is composed only of ash. In a previous study [7], milled FA from the same plant that FA2 originated from was used as a cement replacement material in mortars. Only a small amount (0.2% of the binder's mass) of a superplasticizer was required to achieve the same workability with the control sample, even at a 40% replacement rate. Thus, it is safe to assume that both FAs could be used together with a superplasticizer to replace a significant part of the cement while maintaining good workability.

5. Conclusions

Fly ashes originating from fluidized bed combustion (FBCFA) of peat and wood tend to increase the water demand of cement paste and mortar because of their irregular shape rather than due to chemical characteristics. Milling can significantly improve the packing of these fly ashes by increasing the tapped density, and it lower the water demand of the mortar samples as well as the yield stress and viscosity of the paste samples. The parameter that best correlates with water demand is tapped density, which also correlate well with yield stress and viscosity when using combined data and data for the individual materials. Fly ashes from FBC of peat and wood are recommend to be ground before utilization to enhance workability. In addition, tapped density could be utilized as a robust and simple quality control measurement for FAs in cementitious materials.

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References

[1] V. Sata, C. Jaturapitakkul, K. Kiattikomol, Influence of pozzolan from various by-product materials on mechanical properties of high-strength concrete, Constr. Build. Mater. 21 (2007) 1589–1598. doi:10.1016/j.conbuildmat.2005.09.011.

[2] G. Sheng, J. Zhai, Q. Li, F. Li, Utilization of fly ash coming from a CFBC boiler co-firing coal and petroleum coke in Portland cement, Fuel. 86 (2007) 2625–2631. doi:10.1016/j.fuel.2007.02.018.

[3] R. Rajamma, L. Senff, M.J. Ribeiro, J.A. Labrincha, R.J. Ball, G.C. Allen, V.M. Ferreira, Biomass fly ash effect on fresh and hardened state properties of cement based materials, Compos. Part B Eng. 77 (2015) 1–9. doi:10.1016/j.compositesb.2015.03.019.

[4] Z. Wang, Y. Song, Adsorption properties of CFBC ash–cement pastes as compared with PCC fly ash–cement pastes, Int. J. Coal Sci. Technol. 3 (2016) 62–67. doi:10.1007/s40789-016-0103-8.

[5] J. Zhao, D. Wang, S. Liao, Effect of mechanical grinding on physical and chemical characteristics of circulating fluidized bed fly ash from coal gangue power plant, Constr. Build. Mater. 101, Part 1 (2015) 851–860. doi:10.1016/j.conbuildmat.2015.10.144.

[6] X. Li, Q. Chen, K. Huang, B. Ma, B. Wu, Cementitious properties and hydration mechanism of circulating fluidized bed combustion (CFBC) desulfurization ashes, Constr. Build. Mater. 36 (2012) 182–187. doi:10.1016/j.conbuildmat.2012.05.017.
[7] J. Rissanen, K. Ohenoja, P. Kinnunen, M. Illikainen, Partial replacement of portland-composite cement by fluidized bed combustion fly ash, J. Mater. Civ. Eng. 29 (2017). doi:10.1061/(ASCE)MT.1943-5533.0001899.
[8] J. Payá, J. Monzó, M.V. Borrachero, F. Amahjour, I. Girbés, S. Velázquez, L.M. Ordóñez, Advantages in the use of fly ashes in cements containing pozzolanic combustion residues: silica fume, sewage sludge ash, spent fluidized bed catalyst and rice husk ash, J. Chem. Technol. Biotechnol. 77 (2002) 331–335. doi:10.1002/jctb.583.
[9] X. Fu, Q. Li, J. Zhai, G. Sheng, F. Li, The physical–chemical characterization of mechanically-treated CFBC fly ash, Cem. Concr. Compos. 30 (2008) 220–226. doi:10.1016/j.cemconcomp.2007.08.006.
[10] J.L. Gallias, R. Kara-Ali, J.P. Bigas, The effect of fine mineral admixtures on water requirement of cement pastes, Cem. Concr. Res. 30 (2000) 1543–1549. doi:10.1016/S0008-8846(00)00380-X.
[11] M. Berra, T. Mangialardi, A.E. Paolini, Reuse of woody biomass fly ash in cement-based materials, Constr. Build. Mater. 76 (2015) 286–296. doi:10.1016/j.conbuildmat.2014.11.052.
[12] S. Maschio, G. Tonello, L. Piani, E. Furlani, Fly and bottom ashes from biomass combustion as cement replacing components in mortars production: Rheological behaviour of the pastes and materials compression strength, Chemosphere. 85 (2011) 666–671. doi:10.1016/j.chemosphere.2011.06.070.
[13] A.K.H. Kwan, J.J. Chen, Adding fly ash microsphere to improve packing density, flowability and strength of cement paste, Powder Technol. 234 (2013) 19–25. doi:10.1016/j.powtec.2012.09.016.
[14] S. a. a. M. Fennis, J.C. Walraven, J.A. den Uijl, Compaction-interaction packing model: regarding the effect of fillers in concrete mixture design, Mater. Struct. 46 (2013) 463–478. doi:10.1617/s11527-012-9910-6.
[15] K. Ohenoja, P. Tanskanen, O. Peltosaari, V. Wigren, J. Österbacka, M. Illikainen, Effect of particle size distribution on the self-hardening property of biomass-peat fly ash from a bubbling fluidized bed combustion, Fuel Process. Technol. 148 (2016) 60–66. doi:10.1016/j.fuproc.2016.02.023.
[16] D.-Y. Chen, Y. Yan, Y.-Z. Liu, M. Huang, Influence of mechanically-treatment on physical-chemical properties of circulation fluidized bed combustion fly ash, Key Eng. Mater. 509 (2012) 181–188. doi:10.4028/www.scientific.net/KEM.509.181.
[17] R.J. Deschamps, Using FBC and Stoker Ashes as Roadway Fill: A Case Study, J. Geotech. Geoenvironmental Eng. 124 (1998) 1120.
[18] M. Illikainen, P. Tanskanen, P. Kinnunen, M. Körkkö, O. Peltosaari, V. Wigren, J. Österbacka, B. Talling, J. Niinimäki, Reactivity and self-hardening of fly ash from the fluidized bed combustion of wood and peat, Fuel. 135 (2014) 69–75. doi:10.1016/j.fuel.2014.06.029.
[19] SFS-EN 196-1:2016:en. Methods of testing cement. Part 1: Determination of strength, (2016).
[20] SFS-EN 197-1:en. Cement. Part 1: Composition, specifications and conformity criteria for common cements, (2012).
[21] SFS-EN 451-1:2017:en. Method of testing fly ash. Part 1: Determination of free calcium oxide content, (2017).
[22] SFS-EN 1015-3:en. Methods of test for mortar for masonry. Part 3: Determination of consistence of fresh mortar (by flow table), (1999).
[23] Y. Xia, Y. Yan, Z. Hu, Utilization of circulating fluidized bed fly ash in preparing non-autoclaved aerated concrete production, Constr. Build. Mater. 47 (2013) 1461–1467. doi:10.1016/j.conbuildmat.2013.06.033.
[24] K. Ohenoja, P. Tanskanen, V. Wigren, P. Kinnunen, M. Körkkö, O. Peltosaari, J. Österbacka, M. Illikainen, Self-hardening of fly ashes from a bubbling fluidized bed combustion of peat, forest industry residuals, and wastes, Fuel. (2016). doi:10.1016/j.fuel.2015.10.093.
[25] R. Rajamma, R.J. Ball, L.A.C. Tarelho, G.C. Allen, J.A. Labrincha, V.M. Ferreira, Characterisation and use of biomass fly ash in cement-based materials, J. Hazard. Mater. 172 (2009) 1049–1060. doi:10.1016/j.jhazmat.2009.07.109.
[26] S.V. Vassilev, C.G. Vassileva, Mineralogy of combustion wastes from coal-fired power stations, Fuel Process. Technol. 47 (1996) 261–280. doi:10.1016/0378-3820(96)01016-8.
[27] G. Wang, L. Shen, C. Sheng, Characterization of biomass ashes from power plants firing agricultural residues, Energy Fuels. 26 (2012) 102–111. doi:10.1021/ef201134m.

421 [28] F. Li, J. Zhai, X. Fu, G. Sheng, Characterization of fly ashes from circulating fluidized bed combustion
422 (CFBC) boilers cofiring coal and petroleum coke, Energy Fuels. 20 (2006) 1411–1417.
423 doi:10.1021/ef050377w.
424 [29] D. Gazdič, M. Fridrichová, K. Kulísek, L. Vehovská, The Potential Use of the FBC Ash for the
425 Preparation of Blended Cements, Procedia Eng. 180 (2017) 1298–1305.
426 doi:10.1016/j.proeng.2017.04.292.
427 [30] S.M. Olhero, J.M.F. Ferreira, Influence of particle size distribution on rheology and particle packing of
428 silica-based suspensions, Powder Technol. 139 (2004) 69–75. doi:10.1016/j.powtec.2003.10.004.
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